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(54) Title: PRECIOUS METAL SCAVENGING FROM A LIQUID MEDIUM WITH A FUNCTIONALISED POLYMER FIBER

(57) Abstract: A method for the recovery of a metal from a liquid medium containing the metal I solution or in finely divided insoluble from comprises contacting the medium with a functionalised polymer fibre capable of binding the metal and recovering the metal from the fibre. The polymer fibre is suitably a polyolefin, a fluorinated polyethylene, cellulose or viscose, which is functionalised by the radiation grafting of at least one monomer. The method is particularly suitable for the recovery of platinum group metals from process residues.

## PRECIOUS METAL SCAVENGING FROM A LIQUID MEDIUM WITH A FUNCTIONALISED POLYMER FIBER

This invention relates to a method for the scavenging of metals from liquid media, more particularly to a method for the recovery of platinum group metals (PGMs) from organic, aqueous or mixed organic/aqueous solutions.

The widespread use of noble metals such as PGMs as either heterogeneous or homogeneous catalysts for chemical processes generates substantial amounts of waste solutions or streams of various compositions. The economical use of catalysts based on PGMs is almost always dependent on the efficient recovery of the catalyst, whether by recycling the catalysts themselves, or by the efficient recovery and refining of the noble metal. As is known in the art, the PGMs comprise the lower members of group VIII of the periodic table namely, platinum, palladium, rhodium, iridium, ruthenium and osmium.

Heterogeneous catalysts, in which the noble metal is anchored to a solid support, are often easy to recover by filtration. Loss of metal is mainly due to the loss of fine particulates during filtration or due to solubilisation of the noble metal in the reaction media. The noble metals are usually recovered by incineration and/or leaching procedures and the noble metal is worked up in a conventional manner.

However, the recovery of homogeneous catalysts is not straightforward. If the reaction solution, including reactants, product(s) and solvent, is low boiling and composed only of noble metal compounds, the metal can be concentrated using distillation and the catalysts can possibly be reused several times. If the solution contains other non-noble metal inorganic compounds, salts or high boiling solvents, a useful way of recovery is to add the solution to the smelting process of a noble metal melt. Other ways of treating organic solutions include combustion and pyrolysis however, such processes may give rise to air pollution, especially when phosphorous is present in the work up solutions. Furthermore, losses of precious metals in any pyrometallurgical process can be high as can processing costs, including capital and energy costs.

Processes based on precipitation of the noble metals have been developed. These are based for example, on the recovery of the noble metal by precipitation with elemental sulphur, or sulphur compounds (US 4273578), or with elemental tellurium or reducible tellurium compounds (US 4687514).

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EP 0429017 A1 describes a process to remove rhodium containing catalysts from a solution of hydrogenated nitrile rubber, by passing the residue through an ion-exchange column containing a macroreticular resin modified with a selective amine, thiol, carbodithioate, thiourea and/or dithiocarbamate functional group. From the comparative  
10 examples presented in the patent it is clear that *non*-macroreticular resins, i.e. gel type resins, are unsuccessful in removing rhodium from organic solutions.

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The invention described in US Patent No. 4388279 is concerned with a process for the recovery of trace amounts of noble metals which have been used as catalysts in organic reactions. Products resulting from such reactions are contacted with solid adsorbents selected from Group IA and Group IIA of the Periodic Table, molecular sieves and an ion exchange resins. Examples are given of the performance of calcium carbonate for the recovery of rhodium, but no data are given on the performance of ion exchange resins.

20

US Patent No. 5208194 describes a process for recovering Group VIII transition metal carbonyl complexes by contacting an organic solution with an acidic ion exchange resin containing sulfonic acid groups. Preferred resins are macroreticular or macroporous resins having surface areas greater than about 20 m<sup>2</sup>/g. According to the patent, strongly basic, weakly basic, neutral, and weakly acidic ion exchange resins are unsuitable for use.

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EP 0355837 A2 describes a method for recovery of a transition metal from polar or non-polar liquids, by contacting the liquid with an ion-exchange resin having bonded ionically thereto an organophosphorous ligand. The ligand is ion-exchanged onto traditional ion-exchange resins and the metal to be recovered forms a complex with the ligand.

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EP 0227893 A2 describes a method for the removal of dissolved metals from

solutions using a microporous ethylene polymer with pendant carboxylic acid groups. Comparative examples are described which show that equivalent non-porous materials are not effective. The porosity of the polymer is therefore crucial to the effectiveness of the process described. Furthermore, the polymer does not have equal affinity for similar metals  
5 for example, the affinity is higher for Pd, Ir and Ru than it is for Os, Re and Pt.

Hence, according to the state of the art, macroreticular and porous resins are preferred over gel-type ion-exchangers for recovery of precious metals from organic solutions. However, based on the patent literature, the recoveries obtained with  
10 macroreticular resins are inadequate to allow them to be used commercially in organic solutions. There are also many further problems attached to the use of macroreticular resins in metal scavenging applications from organic solutions. The mechanical stability of porous polymers is often not sufficient to withstand use in stirred reactors without creating fines. Osmotic stability is an even bigger problem since the loading of a homogeneous PGM  
15 complex with attached ligands gives a very high weight increase of the material inducing an osmotic shock that disintegrates the polymer and blocks pores. The porous structure also results in difficulties in further processing of the resins by for example, elution. During elution the material is transferred to an aqueous phase. The treated organic solutions are often viscous and difficult to remove from the porous material. Organic materials will block  
20 the pores of the resin and this material is poorly removed during the elution of the resin. Gel-type materials would hence be preferred. However, traditional gel-type resins function poorly in organic solution mainly due to the large dimensions of the beads, and due to the crosslinks introduced to the materials during preparation of the resins.

25 It is an object of the present invention to develop materials and methods for the easy, efficient and economical recovery of metals from organic solutions. It has now been found that ion-exchange groups attached to fibrous materials show excellent metal binding properties from various organic-based residues, solutions and streams.

30 In accordance with the present invention a method for the recovery of a metal from a liquid medium containing the metal in solution or in finely divided insoluble form comprises

contacting the medium with a functionalised polymer fibre capable of binding the metal; and recovering the metal from the fibre.

5 The present invention has application to organic, aqueous and mixed organic/aqueous media containing metals in metallic or other insoluble form or, preferably, in solution. Such media may be process or effluent streams, or may be streams from the refining of metals, especially the refining of PGMs. The preferred media are those in which a single PGM is present in solution in an organic solvent or a mixed organic/aqueous solvent. Desirably, in the latter case, the organic solvent is miscible with the aqueous system.  
10 Some examples of mixed organic/aqueous media include dimethylformamide/water mixtures, alcohol/water mixtures, where the alcohol may be any liquid alcohol, or acetonitrile/HCl mixtures. Aqueous systems include salt or acid solutions.

15 The metal may be from any group of the periodic table for example, a transition metal, an alkali or alkaline earth metal such as Ca, a heavy metal, or a rare earth metal. Desirably, the metal comprises a transition metal, or a heavy metal such as Hg, Pb or Cd. The transition metal may be noble metal or a base metal active as a catalyst or catalyst promoter such as Ni, Co or W. Most preferably, the metal comprises a noble metal, especially one or more of the PGMs.

20

Preferably, the method further comprises the addition of a precipitating or complexing agent to yield a form of the metal having improved binding characteristics for the functionalised polymer fibre. Suitable precipitating or complexing agents include those selected from the group of thiourea, urea, amines and polyamines.

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Preferably, the polymer is substantially non-porous. The lack of porosity provides the polymers with sufficient mechanical strength to withstand use in stirred reactors without creating fines. Difficulties associated with further processing of the polymers by for example, elution are also mitigated.

30

Preferably, the polymer fibre comprises a polymer chosen from the group; polyolefins, fluorinated polyethylene, cellulose and viscose.

Suitable polyolefins are those formed from units of  $\alpha$ -olefins, the units having the formula  $-\text{CH}_2\text{-CHR}-$ , where R is H or  $(\text{CH}_2)_n\text{CH}_3$  and n is in the range of 0 to 20. Particularly suitable polyolefins are those which are homo- or co-polymers of ethylene and propylene. In the case of fluorinated polyethylenes, those formed from units of the general formula  $-\text{CF}_2\text{-CX}_2-$ , where X is H or F are suitable. For example, polyvinylidene fluoride and polytetrafluoroethylene are particularly preferred.

It has been shown by the present inventors that noble metals or complexes of noble metals can be scavenged from organic or mixed aqueous/organic media using functionalised polymer fibres, that is polymer fibres onto which suitable functional groups have been introduced.

The functional groups can be introduced in various ways including radiation grafting, chemical grafting, chemical modification of pre-formed fibres or further chemical modification of grafted fibres, formation of interpenetrating networks etc. Preferably, the functional groups are introduced by radiation grafting.

Graft copolymers can be prepared in various ways but radiation grafting is an especially suitable method for graft modification of polymer fibres. Radiation grafting is generally known, and involves the irradiation of a polymer in a suitable form, for example, film, fibre, pellets, hollow fibre, membrane or non-woven fabric, to introduce reactive sites (free radicals) into the polymer chain. These free radicals can either combine to give cross-links, as is the case for polyethylene, or cause chain scission as is the case for polypropylene. On the other hand, the free radicals can be utilised to initiate graft copolymerisation under specific conditions. Three different methods of radiation grafting have been developed; 1) direct radiation grafting of a vinyl monomer onto a polymer (mutual grafting); 2) grafting on radiation-peroxidized polymers (peroxide grafting); and 3) grafting initiated by trapped radicals (pre-irradiation grafting). Pre-irradiation grafting is mostly preferred since this method produces only small amounts of homopolymer in comparison to mutual grafting.

Preferably, the functionalised polymer fibre comprises at least one functional group selected from; carboxylic, sulphonic, pyridinium, isothiuronium, phosphonium, amine,

thiol or the like, and grafted vinyl monomers such as acrylic acid, methacrylic acid, acrylates, methacrylates, styrene, substituted styrenes such as  $\alpha$ -methyl styrene, vinyl benzyl derivatives such as vinyl benzyl chloride, vinyl benzyl boronic acid and vinyl benzyl aldehyde, vinyl acetate, vinyl pyridine, and vinyl sulphonic acid.

5

The functionalised fibres may be added to the solution to be treated in a stirred tank or the solution to be treated may be passed through a column packed with the fibres. It may be advantageous to heat the solution for example, in the range from ambient to 100°C.

10

In the present invention, fibres may be used without further processing and be of any length however, they have the very substantial advantage over polymer beads in that they may be converted, using conventional technology, into a great variety of forms. Thus, fibres may be spun, woven, carded, needle-punched, felted or otherwise converted into threads, ropes, nets, tows or woven or non-woven fabrics of any desired form or structure. Fibres can easily be stirred in a liquid medium, and filtered off or otherwise separated therefrom. If desired, fibres of different characteristics can readily be combined in threads or fabrics, in order to optimise the metal scavenging properties for a particular feedstock medium. In an embodiment, fibres may be combined with inorganic fibres such as silica or alumina fibres in order to provide increased mechanical strength. This may be of use when the fibres are used in processes which involve high degrees of agitation or high turbulence.

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The noble metal may be recovered by filtering the fibres from the solution and recovering the noble metal by eluting the fibres using an ion-displacing reagent such as a strong acid or salt or a complexing agent, e.g. a sodium salt, or by destroying the fibre structure, e.g. using pyrolysis or hydrolysis, to produce a metal concentrate. The concentrate can then be worked up in a conventional manner.

25

The invention will now be described by way of non-limiting example only, and it will be appreciated that skilled person will readily see many opportunities to use the present invention in all its aspects.

30

**EXAMPLE 1**

Polyethylene fibres were irradiated under inert atmosphere to total dose of 150 kGy using an electron accelerator operating at an acceleration voltage of 175 kV and beam  
5 current of 5 mA. The irradiated fibres were immediately immersed in a reaction mixture containing styrene, vinyl benzyl chloride and ethanol. The reaction mixture was purged with nitrogen before initiating the reaction and the grafting reaction was allowed to continue to completion, which usually took approximately 6 hours.

10 The resulting fibres were filtered from the reaction solution and washed firstly with ethanol and then with dichloroethane.

**EXAMPLE 2**

15 Polyethylene fibres were irradiated under an inert atmosphere to total dose of 150 kGy using an electron accelerator operating at an acceleration voltage of 175 kV and beam current of 5 mA. The irradiated fibres were immediately immersed in a reaction mixture containing 4-vinyl pyridine and ethanol. The reaction mixture was purged with  
20 nitrogen before initiating the reaction and the grafting reaction was allowed to continue to completion, which usually took approximately 6 hours. The resulting fibres were filtered from the reaction solution and washed firstly with ethanol and then with dichloroethane or with a dilute aqueous acid.

**EXAMPLE 3**

25 Polyethylene fibres were irradiated under an inert atmosphere to total dose of 150 kGy using an electron accelerator operating at an acceleration voltage of 175 kV and beam current of 5 mA. The irradiated fibres were immediately immersed in a reaction mixture containing styrene and ethanol. The reaction mixture was purged with nitrogen  
30 before initiating the reaction and the grafting reaction was allowed to continue to completion, which usually took approximately 6 hours. The resulting fibres were filtered from the reaction solution and washed firstly with ethanol and then with dichloroethane.



**EXAMPLE 4**

100g fibres prepared as in Example 1 were stirred in ethanol for 1 hour. 20g of thiourea dissolved in ethanol was added and the stirring continued for a further 2 hours.

5 The fibres were filtered from the solution and washed with ethanol before further use.

**EXAMPLE 5**

10 Fibres prepared as in Example 3 were added to a solution of dichloroethane and left overnight. Chlorosulphonic acid was added under stirring and the stirring continued for 5 hours. The fibres were filtered from the solution and treated with 2M sodium hydroxide solution, washed with acidified water to pH 1, and finally washed repeatedly with distilled water.

**EXAMPLE 6**

15 130g of an oxo-ester residue containing 395 ppm of palladium was dissolved in a dimethyl formamide/water mixture. Fibres prepared as in Example 2 were added to the solution and the dispersion stirred over night at room temperature. The palladium content of the solution decreased to 40 ppm.

**EXAMPLE 7**

25 The same solution as used in Example 6 was stirred at room temperature over night with fibres prepared as in Example 4. The palladium content of the solution decreased to 3 ppm.

**EXAMPLE 8**

30 A glass column was packed with fibres prepared as in Example 2. The same solution as in Example 6 was passed through the column. An ash content of 4 % by weight, analysed as Pd, was achieved and less than 3 ppm Pd remained in solution.

**EXAMPLE 9**

5 A carbonylation residue solution containing 105 ppm of rhodium was stirred with fibres prepared as in Example 5. The rhodium content of the solution decreased to approximately 50 ppm when the solution was boiled in presence of the fibres.

**EXAMPLE 10**

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The same solution as in Example 9 was stirred with fibres prepared as in Example 4. The rhodium content of the solution decreased to 45 ppm when stirred over night at 60°C. However, when thiourea in ethanol was added to the solution and stirring continued at 60°C for approximately 2 hours the rhodium content of the solution decreased to 3 ppm.

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**EXAMPLE 11**

20 Thiourea dissolved in ethanol was added to a hydroformylation residue solution containing 850 ppm of rhodium. Fibres prepared as in Example 5 were added to the solution under stirring. After 1 hour, the rhodium content of the solution decreased to 20 ppm. When DMF was used instead of ethanol, the rhodium content of the solution decreased to 10 ppm under similar reaction conditions.

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**EXAMPLE 12**

30 A high boiling point distillation residue from a coupling reaction containing 4.5 % palladium and 4.5 % phosphorus, present as a triaryl phosphine, was dissolved in an ethanol/thiourea mixture under reflux. Fibres prepared as in Example 5 were added to the solution and stirred for 60 minutes. Approximately 97-99 % of the palladium was recovered on the fibres.

**EXAMPLE 13**

A carbonylation residue containing 105 ppm of rhodium was used for a comparative trial of fibres versus a commercially-available strong acid cation exchanger ("Amberlyst").

- 5 This bead form ion-exchange material contains the same sulfonic acid functionality as the fibre prepared in Example 5. 80 ml ethanol containing 2 g thiourea was added to 200 ml of the carbonylation residue and heated at 60°C for 30 minutes. To half of this solution, 2 g of dry Amberlyst beads were added and stirred at 60°C for 2h. To the other half of the solution, 2g of dry fibres prepared as in Example 5 were added and stirred at 60°C for 2h.
- 10 The recovery of rhodium for the Amberlyst beads was found to be 43%, compared with 98.5% for the scavenging fibres according to Example 5.

**EXAMPLE 14**

- 15 Fibres prepared according to example 4 were further treated by stirring for 2 hours in an ethanol solution containing 2M sodium hydroxide. The fibres were filtered from this solution, washed with distilled water and treated with acid to pH 1. The fibres were re-filtered and washed with distilled water to neutral pH.

**EXAMPLE 15**

- 20 Fibres prepared according to example 14 were immersed in a reaction residue from a coupling reaction which contained THF, triaryl phosphines and 30 ppm of palladium. The fibres and residue were refluxed for 1 hour, after which time no palladium was detectable in the reaction residue.
- 25

**CLAIMS**

1. A method for the recovery of a metal from a liquid medium containing the metal in solution or in finely divided insoluble form, the method comprising contacting the medium  
5 with a functionalised polymer fibre capable of binding the metal; and recovering the metal from the fibre.
2. A method according to claim 1, wherein the liquid medium comprises an organic, aqueous or mixed organic/aqueous medium.
- 10 3. A method according to claim 1 or claim 2, wherein the medium is a process residue or stream comprising catalyst residues or catalyst, an effluent stream or a refining stream from the refining of metals.
- 15 4. A method according to any preceding claim, wherein the metal comprises a transition metal or a heavy metal.
5. A method according to claim 4, wherein the metal comprises a PGM.
- 20 6. A method according to any preceding claim, further comprising the addition of a precipitating or complexing agent to yield a form of the metal having improved binding characteristics for the functionalised polymer fibre.
- 25 7. A method according to claim 6, wherein the precipitating or complexing agent comprises at least one from the group of thiourea, urea, amines and polyamines.
8. A method according to any preceding claim, wherein the polymer fibre is substantially non-porous.
- 30 9. A method according to any preceding claim, wherein the polymer fibre comprises a polymer chosen from the group; polyolefins, fluorinated polyethylene, cellulose and viscose.

10. A method according to any preceding claim, wherein the functionalised polymer fibre comprises at least one functional group selected from; carboxylic, sulphonic, pyridinium, isothiuronium, phosphonium, amine, thiol, grafted vinyl monomers, acrylic acid, methacrylic acid, acrylates, methacrylates, styrene, substituted styrenes,  $\alpha$ -methyl  
5 styrene, vinyl benzyl derivatives, vinyl benzyl chloride, vinyl benzyl boronic acid, vinyl benzyl aldehyde, vinyl acetate, vinyl pyridine, and vinyl sulphonic acid.
11. A method according to claim 10, wherein the at least one functional group is introduced by radiation grafting.
- 10 12. A method according to any preceding claim, wherein the metal is recovered by eluting with an ion-displacing reagent such as a strong acid or salt or complexing agent.
13. A method according to any of claims 1 to 11, wherein the metal is recovered by  
15 destroying the fibre by pyrolysis or hydrolysis.

## INTERNATIONAL SEARCH REPORT

 In International Application No  
 PCT/GB 01/04540

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B3/24 C22B11/00 C22B3/42 C22B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 117 (C-487), 13 April 1988 (1988-04-13) & JP 62 238337 A (NICHIBI:KK), 19 October 1987 (1987-10-19) abstract	1-5, 12
A	abstract	9, 10
X	DATABASE WPI Section Ch, Week 199315 Derwent Publications Ltd., London, GB; Class A97, AN 1993-120582 XP002192311 "heavy metal ion or colloid removal from water for treatment" & JP 05 057280 A (JAPAN ATOMIC ENERGY RES INST), 9 March 1993 (1993-03-09) abstract	1-4, 9-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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## INTERNATIONAL SEARCH REPORT

 In International Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 391 (C-537), 18 October 1988 (1988-10-18) & JP 63 135432 A (JAPAN ATOM ENERGY RES INST), 7 June 1988 (1988-06-07) abstract -& DATABASE WPI Week 198828 Derwent Publications Ltd., London, GB; AN 1988-195876 XP002192319 "fibrous ion exchange material prepn." & JP 63 135432 A, 7 June 1988 (1988-06-07) abstract	1,2,9-11
X A	US 4 500 396 A (D AGOSTINO VINCENT F ET AL) 19 February 1985 (1985-02-19) abstract column 1, line 4 - line 25 column 2, line 3 - line 45 column 2, line 56 - column 3, line 3 column 3, line 35 - line 59 column 4, line 49 - line 53 claims 1-4,7	1-5,9-12 6,7
X A	US 4 543 169 A (D AGOSTINO VINCENT F ET AL) 24 September 1985 (1985-09-24) abstract column 1, line 4 - line 14 column 2, line 6 - column 3, line 2 column 3, line 61 - line 66 claims 1-3,6,11,12,14-16	1-5,9-12 6,7
X A	EP 0 227 893 A (DOW CHEMICAL CO) 8 July 1987 (1987-07-08) cited in the application abstract page 2, line 1 - line 3 page 3, line 21 - line 33 page 3, line 47 - page 4, line 40 page 5, line 12 - line 40 page 6, line 4 - line 30 page 7, line 16 - line 21 page 7, line 46 - page 8, line 14 claims 1,2,5,7,9; examples 7,10,11,13,16,26	1-5,9, 10,12 6,8,13
X A	US 4 092 250 A (SANO TAKEZO ET AL) 30 May 1978 (1978-05-30) abstract column 1, line 5 - line 6 column 1, line 40 - line 65 column 2, line 27 - column 3, line 2 column 3, line 33 - line 44 claims 1,4,5; examples	1-5,9,10 11
	-/--	

## INTERNATIONAL SEARCH REPORT

In International Application No  
PCT/GB 01/045405

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 011, no. 282 (C-446), 11 September 1987 (1987-09-11) &amp; JP 62 083006 A (ASAHI CHEM IND CO LTD), 16 April 1987 (1987-04-16) abstract -&amp; DATABASE WPI Week 198721 Derwent Publications Ltd., London, GB; AN 1987-146391 XP002192320 "Mfr. of cation selective absorption material" &amp; JP 62 083006 A (ASAHI CHEM IND CO LTD), 16 April 1987 (1987-04-16) abstract</p>	9-11
A	<p>US 4 386 006 A (HARRINGTON DONALD F) 31 May 1983 (1983-05-31) column 1, line 21 - line 37</p>	9, 10
A	<p>DATABASE WPI Section Ch, Week 197748 Derwent Publications Ltd., London, GB; Class A18, AN 1977-85311Y XP002192321 &amp; JP 52 123986 A (TORAY IND INC), 18 October 1977 (1977-10-18) abstract</p>	10
A	<p>DATABASE WPI Section Ch, Week 197834 Derwent Publications Ltd., London, GB; Class M11, AN 1978-61630A XP002192312 &amp; SU 311 534 A (MOSC TEXTILE INST), 25 November 1977 (1977-11-25) abstract</p>	13



# INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No  
PCT/GB 01/04540

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 62238337	A	19-10-1987	NONE	
JP 5057280	A	09-03-1993	NONE	
JP 63135432	A	07-06-1988	JP 1865131 C JP 5080941 B	26-08-1994 10-11-1993
US 4500396	A	19-02-1985	JP 1660179 C JP 3020447 B JP 60221537 A	21-04-1992 19-03-1991 06-11-1985
US 4543169	A	24-09-1985	NONE	
EP 0227893	A	08-07-1987	US 4747957 A US 4747954 A US 4661634 A AT 87981 T AU 600673 B2 AU 6263286 A CA 1284844 A1 DE 3688240 D1 DE 3688240 T2 DK 170018 B1 EP 0227893 A2 ES 2001786 A6 JP 2529673 B2 JP 62068505 A KR 9404630 B1 NO 173370 C NZ 217571 A ZA 8607001 A CA 1283984 A1 CA 1265535 A1	31-05-1988 31-05-1988 28-04-1987 15-04-1993 23-08-1990 19-03-1987 11-06-1991 13-05-1993 11-11-1993 01-05-1995 08-07-1987 16-06-1988 28-08-1996 28-03-1987 27-05-1994 08-12-1993 27-07-1989 25-05-1988 07-05-1991 06-02-1990
US 4092250	A	30-05-1978	JP 52022172 A CA 1066439 A1 DE 2635824 A1 FR 2320906 A1 GB 1547613 A	19-02-1977 13-11-1979 24-02-1977 11-03-1977 27-06-1979
JP 62083006	A	16-04-1987	JP 2077963 C JP 7114945 B	09-08-1996 13-12-1995
US 4386006	A	31-05-1983	NONE	
JP 52123986	A	18-10-1977	JP 1249709 C JP 59023852 B	25-01-1985 05-06-1984
SU 311534	A	25-11-1977	SU 311534 A1	25-11-1977